Equilibrium Cluster Phases and Low-Density Arrested Disordered States: The Role of Short-Range Attraction and Long-Range Repulsion

Francesco Sciortino,[1] Stefano Mossa,[1,2] Emanuela Zaccarelli,[1] and Piero Tartaglia[1]

[1]*Dipartimento di Fisica and INFM Udr and Center for Statistical Mechanics and Complexity, Università di Roma "La Sapienza,"*
Piazzale Aldo Moro 2, I-00185, Roma, Italy
[2]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble CEDEX, France*

We study a model in which particles interact with short-ranged attractive and long-ranged repulsive interactions, in an attempt to model the equilibrium cluster phase recently discovered in sterically stabilized colloidal systems in the presence of depletion interactions. At low packing fractions, particles form stable equilibrium clusters which act as building blocks of a cluster fluid. We study the possibility that cluster fluids generate a low-density disordered arrested phase, a gel, via a glass transition driven by the repulsive interaction. In this model the gel formation is formally described with the same physics of the glass formation.

Gels are disordered arrested systems capable of sustaining weak shear stress. Although commonly used in food, cosmetics, and detergents, the physical processes involved in the transformation of a solution capable of flowing into a highly viscous substance, and eventually into a gel state, are far from being understood. The gel state can be generated via several routes. Interrupted phase separation, bond percolation, irreversible diffusion limited aggregation, and attractive glass transition have been suggested as possible mechanisms for gel formation in polymeric and colloidal systems.

Sterically stabilized colloidal systems have often been used as an experimental realization of the hard-sphere model, to study both fluid-crystal transition and glass formation. The addition of small polymers in solution modifies the effective colloid-colloid interaction by depletion mechanisms, complementing the hard-sphere repulsion with a short-range attraction, on a length scale of the order of a few percent of the colloid size.

At small volume fractions ϕ and low temperature T, the systems experience dynamic arrest in a transient gel structure [1,2]. Recent experiments suggest that the gel region in the $(\phi - T)$ plane is contiguous to a cluster phase, in which particles form freely diffusing clusters of finite size [3–5]. Studies of the phase diagram of short-ranged (uncharged) attractive colloidal systems show that these systems are characterized by fluid and crystal phases and by a very flat metastable liquid-gas spinodal, which extends to considerably low values of ϕ [6–8]. In simulations of short-ranged attractive potentials, gel phases have only been observed as a result of an arrested phase separation, but with no contiguity with an equilibrium cluster phase [9].

In this Letter, we provide evidence, via molecular dynamics (MD) simulations that, when short-range attractive interactions are complemented by long-range repulsive interactions, equilibrium cluster phases, as well as disordered arrested states contiguous to cluster phases, can be generated. The long-range repulsive interactions may arise from screened electrostatic interactions or from effective interactions accounting for the presence of cosolutes in solution [10,11].

The possibility of generating a cluster phase, i.e., an equilibrium state in which colloidal particles partition into stable clusters via the competition between attraction (which favors cluster growth at low T) and long-range repulsion (which favors low local particle densities and, therefore, small aggregates), has been discussed in previous theoretical works [12–15]. Here we show that in the presence of an appropriate balance between attraction and repulsion the system forms stable clusters, around an optimal cluster size. To quantify this proposition, we calculate the ground state energy of clusters of different size [16,17] for the case of particles interacting with a potential $V(r)$ which is the sum of a short-range attractive potential V_{SR} (modeled for simplicity with the generalization to very large α of the Lennard-Jones $2\alpha - \alpha$ potential, as proposed by Vliegenthart *et al.* [6]),

$$V_{SR}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{2\alpha} - \left(\frac{\sigma}{r} \right)^{\alpha} \right], \qquad (1)$$

and of a screened electrostatic repulsive interaction V_Y (modeled by a Yukawa potential),

$$V_Y(r) = A \frac{e^{-r/\xi}}{r/\xi}. \qquad (2)$$

In the following, the parameters ϵ and σ entering in V_{SR} are chosen as units of energy and distance. The parameter α has been chosen equal to 100, corresponding to an attractive range of about 3% of σ (see inset of Fig. 1). For this value of α, the liquid-gas critical temperature for V_{SR} is found to be 0.235 ± 0.005. Figure 1 shows that the cluster ground state energy, for particles interacting with
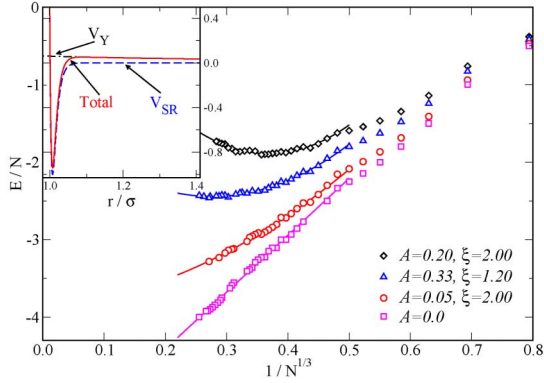
FIG. 1 (color online). Ground state energy for connected clusters composed of N particles for different choices of A and ξ, with $\alpha = 100$. While in the $A = 0$ case a monotonous decrease of the energy—linear in $N^{-1/3}$ as expected from the balance between bulk and surface effects—is found, for large A the lowest energy state is reached for a finite N^* value, which provides an upper limit to the size of thermodynamically stable clusters. The inset shows V_{SR}, V_Y, and their sum for the case $A = 0.05$ and $\xi = 2$.

the potential $V_{SR} + V_Y$ for appropriate values of A and ξ, has a minimum at a finite size N^*, indicating that clusters of size larger than N^* are energetically disfavored (and, hence, that liquid condensation is inhibited). Since entropic contributions to the free energy will always favor small clusters, aggregation will never proceed beyond N^*. The existence of an optimal cluster size (which will of course depend on T and ϕ) suggests that, at low T, clusters act as building blocks of the supramolecular cluster fluid.

The cluster-cluster interaction is essentially controlled by the Yukawa repulsion, due to the short-range nature of the attractive part of the potential. It can be calculated analytically, if one approximates the cluster to a sphere of radius R composed of a homogeneous density ρ of points interacting via the potential V_Y [Eq. (2)]. The resulting cluster-cluster interaction is, again, of the Yukawa type with the same ξ but a renormalized amplitude $A(R)$:

$$\frac{A(R)}{A} = \left\{ 2\pi\xi^3 \rho e^{-R/\xi} \left[1 + \frac{R}{\xi} + \left(\frac{R}{\xi} - 1 \right) e^{2R/\xi} \right] \right\}^2. \quad (3)$$

Therefore, aggregation of particles into clusters of size N (and radius $R \sim N^{1/3}$) has two effects: (i) renormalization of the amplitude of the interaction, and (ii) decrease of the cluster number density n according to

$$\frac{n(R)}{n} = \frac{1}{N}. \quad (4)$$

Since ξ is not modified, the aggregation process can be seen as the generator of a flow, defined via Eqs. (3) and (4), in the phase diagram of the pure repulsive Yukawa potential.

Figure 2 shows an extended phase diagram for the pure Yukawa potential. Together with the fluid-crystal coexistence lines, previously calculated by Robbins *et al.* [18], and Meijer and Frenkel [19], we show an isodiffusivity curve [20] (i.e., the locus of the point with the same diffusion constant) and the ideal glass line, evaluated within the mode coupling theory [21] (MCT) using *exact* numerical structure factors as input. The latter curve provides an upper limit to the glass transition line. It is important to note that the long-range nature of the repulsion enables the formation—at low $k_B T/A$ values—of solid phases with extremely low density (named Wigner crystal or Wigner glass [22–24]).

An example of the flow in the Yukawa phase diagram induced by clustering is shown in Fig. 2. The starting point is assumed to be a system composed of monomers ($N = 1$) interacting via the potential $V_{SR} + V_Y$. If T is sufficiently low, a clustering phenomenon will take place, driven by the attractive part of the potential. Such an aggregation process acts as a generator of a flow in the phase diagram, moving the system, due to the effective increase of the repulsive amplitude [Eq. (3)] and to the associated decrease of the cluster number density [Eq. (4)], closer and closer to the melting and glass lines. If the optimal size is reached before crossing the melting line, the equilibrium state for the system will correspond
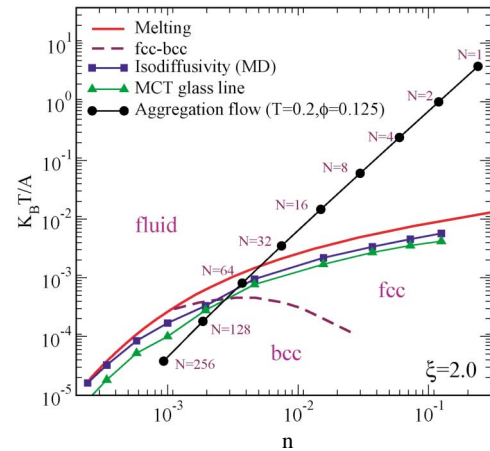

FIG. 2 (color online). Extended phase diagram for the Yukawa potential, for $\xi = 2$, reporting the fluid-crystal phase boundary lines [18], the isodiffusivity locus ($D = 10^{-4}$ in units of $\sqrt{A\xi^2/m}$), and the ideal MCT glass line. The flow line, calculated according to Eqs. (3) and (4), describes a system of Yukawa particles ($A = 0.05$, $\xi = 2$), with packing fraction $\phi = \pi/6\sigma^3 n = 0.125$ and $T = 0.20$, assumed to progressively form spherical homogeneous clusters of size 1, 2, 4, 8,..., 128. When the cluster size reaches $N \approx 47$, the melting line is crossed and the fluid transforms into a fcc crystal whose elementary units are clusters of that size. If crystallization is avoided, the ideal MCT glass line is crossed when the average cluster size reaches $N \approx 86$. These figures are in very good agreement with the simulation data shown in Fig. 3.

to a fluid phase of clusters. In the other case, an arrest phenomenon will take place, driven by the crystallization or—more likely because of the inherent self-generated cluster polydispersity—by a glass transition. With this mechanism arrested disordered states with small ϕ can be generated. This new route to the gel state demonstrates, in the case of weakly charged short-ranged attractive colloids, the identity of the gel and the glass states of matter.

We next provide numerical evidence that the above-proposed mechanism does lead to disordered arrested states contiguous to a cluster phase. We perform MD simulations of particles interacting with the potential $V_{SR} + V_Y$ [25], both along a constant T and along a constant ϕ path. Here, we focus on the specific choice of $A = 0.05$ and $\xi = 2$, referring to future publications for a more extensive analysis. This choice of parameters is characteristic of colloidal particles in weakly polar solvents [4,26,27].

The cluster size distribution, shown in Fig. 3, provides a characterization of the clustering process. While at high T the cluster size is monotonically decreasing, around $k_B T/\epsilon = 0.2$ the distributions develop a peak at a finite value, signaling the presence of stable equilibrium aggregates composed of 20–30 particles. We note that such a resulting cluster phase can be considered as an echo of the interrupted spinodal decomposition, since clustering takes places just below the liquid-gas critical temperature of the bare V_{SR} potential.

For each of the studied T, the unclustered system ($N = 1$) can be represented as a point in Fig. 2. A flow curve, starting from each of these points, can be calculated according to Eqs. (3) and (4). In this way, a theoretical prediction for the average cluster size at which crystallization and (MCT) vitrification are expected can be
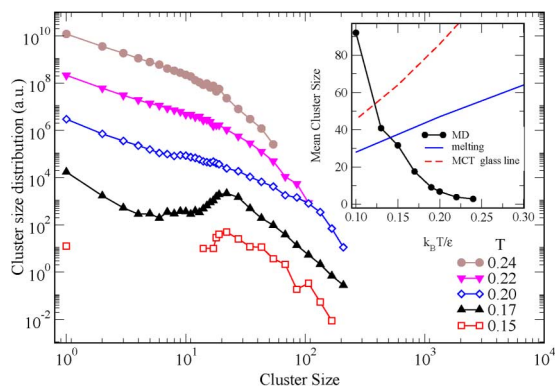
derived. Such curves are shown in the inset together with the T dependence of the average cluster size calculated from the MD data. For the present choice of A, ξ, and ϕ, structural arrest (either in the form of crystallization or in the form of vitrification) is predicted when the average cluster size is $\gtrsim 35$ particles ($k_B T/\epsilon \lesssim 0.15$).

Before turning to the evaluation of dynamical properties, we discuss the evolution of the structure with T, analyzing the static structure factor $S(q)$. As shown in Fig. 4(a), $S(q)$ progressively develops a peak at wave vectors q associated with distances in real space of the order of several particle diameters, reflecting the nearest neighbor cluster-cluster distance. The amplitude of this novel peak changes significantly in a small temperature range around the T region where the flow diagram predicts the crossing of the crystallization line. Therefore, the system changes from a solution of interacting particles toward a system of larger and larger interacting clusters. In the cluster phase, the location of the peak changes very weakly both with T and with ϕ. It is interesting to note that both the location and the amplitude of the cluster-cluster peak are in agreement with the experimental data for colloidal gels reported in Ref. [3]. To confirm that the aggregation process indeed generates a disordered arrested state, we show in Fig. 4(b) the coherent scattering function $F(q, t)$. It displays a (one-step) decay, with a characteristic time which increases on cooling. At the lowest studied T, the correlation function does not decay to zero, signaling that the system is

FIG. 3 (color online). Cluster size distribution, on a log-log scale, for $\phi = 0.125$. For clarity, curves for different T have been shifted along the vertical axis progressively by one decade. The inset shows the T dependence of the average cluster size. It also shows, for each T, the size at which the crystallization and the ideal glass transition lines are crossed, according to the flow described in Fig. 2.
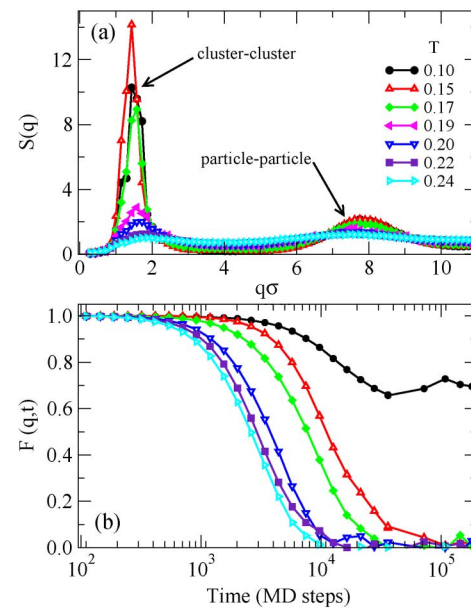
FIG. 4 (color online). Evolution of static and dynamic quantities on cooling at $\phi = 0.125$. (a) $S(q)$. Note the development of a peak at small q, reflecting the formation of clusters in the system. (b) $F(q, t)$ at $q\sigma = 2.7$. At $T = 0.1$, the autocorrelation function does not decay to zero any longer, highlighting the formation of a structurally arrested phase.

trapped in a nonergodic state. The transition from fluid to glass is very sharp, again in full agreement with results for colloidal gels [3].

In summary, we have proposed and studied a model which shows equilibrium cluster phases and arrested states at low densities, opening the way for accurate comparisons between experiments and theoretical predictions. Contrary to what has been proposed before for attractive colloids, we suggest that, in these systems, the gel phase is not stabilized by the short-range attraction (and, hence, its formation is not connected to the attractive glass transition observed at high packing fractions [28]). The simulation data (Figs. 3 and 4) show that the competition between isotropic short-range attraction and long-range repulsion—of the type found in colloidal systems and in protein solutions [29,30]—is capable of generating a very rich range of phenomena [31]. Within the present model, the formation of low density arrested states can be modeled as a glass transition, where clusters (as opposed to particles) are trapped in cages generated by the long-range repulsions. It will be interesting to study if the arrested disordered state is metastable with respect to a fcc or a bcc crystal of "spherical" clusters (a Wigner crystal) or with respect to lamellar phases, which has been observed in related models [12,13,15].

---

[1] W. C. Poon *et al.*, Physica A (Amsterdam) **235**, 110 (1997).

[2] N. A. M. Verhaegh *et al.*, Physica A (Amsterdam) **264**, 64 (1999).

[3] P. N. Segrè *et al.*, Phys. Rev. Lett. **86**, 6042 (2001).

[4] A. D. Dinsmore and D. A. Weitz, J. Phys. Condens. Matter **14**, 7581 (2002).

[5] H. Sedgwick *et al.*, cond-mat/0309616.

[6] G. A. Vliegenthart *et al.*, Physica A (Amsterdam) **263**, 378 (1999).

[7] V. J. Anderson and H. N. W. Lekkerkerker, Nature (London) **416**, 811 (2002).

[8] M. A. Miller and D. Frenkel, Phys. Rev. Lett. **90**, 135702 (2003).

[9] E. Zaccarelli *et al.*, cond-mat/0310765.

[10] A. A. Louis *et al.*, Phys. Rev. E **65**, 061407 (2002).

[11] C. N. Likos, Phys. Rep. **348**, 267 (2002).

[12] D. Wu *et al.*, J. Phys. Chem. **96**, 4077 (1992).

[13] R. P. Sear *et al.*, Phys. Rev. E **59**, R6255 (1999).

[14] J. Groenewold and W. K. Kegel, J. Phys. Chem. B **105**, 11702 (2001).

[15] C. B. Muratov, Phys. Rev. E **66**, 066108 (2002).

[16] D. J. Wales and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997).

[17] To evaluate the lowest energy minima, we have implemented a modified version of the basin-hopping algorithm introduced by Wales and Doye [16]. The algorithm consists of a constant-T Monte Carlo (MC) simulation where the acceptance criterion is based upon the energy of the closest minimum of the potential energy surface. To favor barrier crossing, every 100 MC steps the least bounded atom is removed and reinserted in the position with lowest insertion energy. In the search, moves creating disconnected clusters are rejected. Indeed, for $N \gtrsim N^*$, the ground state consists of separated noninteracting clusters.

[18] M. O. Robbins *et al.*, J. Chem. Phys. **88**, 3286 (1988).

[19] E. J. Meijer and D. Frenkel, J. Chem. Phys. **94**, 2269 (1991).

[20] MD simulation of 1000 particles of mass m interacting with the Yukawa potential [Eq. (2)] are performed for ten different number densities, to evaluate the T dependence of D and $S(q)$. Iso-D curves for $D < 10^{-4}\sqrt{A\xi^2/m}$ cannot be calculated, since crystallization takes place. The MCT equations [21] are solved with standard techniques on a grid of 250 wave vectors, to evaluate the ideal glass transition line.

[21] W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991), p. 287.

[22] S. K. Lai *et al.*, Phys. Rev. E **56**, 766 (1997).

[23] J. Bosse and S. D. Wilke, Phys. Rev. Lett. **80**, 1260 (1998).

[24] D. Bonn *et al.*, Europhys. Lett. **45**, 52 (1999).

[25] Data reported in Figs. 3 and 4 refer to a system of $N_o = 2500$ particles of unit mass m, interacting via the potential $V = V_Y + V_{SR}$ defined in Eqs. (1) and (2). The parameters of V_Y are $A = 0.05$ and $\xi = 2$. The potential has been cut off at 8σ; such a large cutoff is necessary to properly account for the long-range nature of V_Y. Time is measured in units of $\sqrt{m\sigma^2/\epsilon}$. The integration time step is 4.55×10^{-4} time units. The equilibration dynamics, performed in the NVT ensemble, is extremely slow, and often requires more than 10^8 integration time steps. In all cases, MD runs were performed starting from equilibrium configurations at $k_B T/\epsilon = 1$. At very low T, equilibrium is not reached and the system remains trapped in an arrested state. After equilibration, NVE runs are performed to evaluate $F(q, t)$, defined as $\langle \rho^*(\mathbf{q}, t)\rho(\mathbf{q}, 0)\rangle/S(q)$, where $\rho(\mathbf{q}, t) = (1/\sqrt{N_o})\sum_i e^{i\mathbf{q}\mathbf{r}^i(t)}$, $\mathbf{r}^i$ are the coordinates of particle i at time t, and $S(q) \equiv \langle|\rho(\mathbf{q}, 0)|^2\rangle$. To calculate cluster size properties, a bond between two particles is defined when the relative distance is less than 1.05σ (value at which $V_{SR} = -0.03\epsilon$).

[26] A. Yethiraj and A. van Blaaderen, Nature (London) **421**, 513 (2003).

[27] J. C. Crocker and D. G. Grier, Phys. Rev. Lett. **73**, 352 (1994).

[28] J. Bergenholtz *et al.*, Langmuir **19**, 4493 (2003); J. Bergenholtz and M. Fuchs, Phys. Rev. E **59**, 5706 (1999).

[29] R. Piazza, Curr. Opin. Colloid Interface Sci. **5**, 38 (2000).

[30] G. Pellicane *et al.*, J. Phys. Condens. Matter **15**, 375 (2003).

[31] J. Dudowicz *et al.*, Phys. Rev. Lett. **92**, 045502 (2004), and references therein.